

obtained on connecting the two mercury cups by a wire, the current passing could be modified at will, and shown to exhibit all the ordinary phenomena of moderately weak currents.

After continued action with small resistance only in circuit, the liquid in the funnel was found on analysis to contain no copper whatever, whilst that surrounding the copper plate, though colourless before removal from the tube, speedily became blue on exposure to air, and contained more or less considerable amounts of copper in solution, obviously originally in the condition of *cuprous* oxide,  $\text{Cu}_2\text{O}$ .

Following up the ideas suggested by the above observations, we are making a number of experiments with a variety of analogous combinations, in which atmospheric oxidation constitutes the essential chemical action taking place; by varying the nature of the aëration plates, the metals dissolved, and the liquids employed (as also by substituting other gases, *e.g.*, chlorine, for air), a large number of combinations are obviously obtainable. Some of those which we have so far examined present points of considerable interest, the oxidising action exerted under favourable conditions being strongly marked, so much so that certain metals, *e.g.*, mercury and silver, not ordinarily prone to atmospheric oxidation, can under suitable conditions be gradually oxidised and dissolved in appropriate liquids, just as the copper is dissolved in the ammonia in the cell above described; these actions, moreover, being accompanied by the development of currents of strength sufficient to cause measureable amounts of electrolytic decomposition outside the cell, *e.g.*, in a silver voltameter.

II. "Clausius's Formula for the Change of State from Liquid to Gas applied to Messrs. Ramsay and Young's Observations on Alcohol." By GEO. FRAS. FITZGERALD, M.A., F.T.C.D., F.R.S., Erasmus Smith's Professor of Natural and Experimental Philosophy in the University of Dublin. Received March 14, 1887.

Clausius, in Wiedemann's 'Annalen,' vol. 14, 1881, pp. 279—290, and 'Phil. Mag.,' vol. 12, 1881, p. 381, and vol. 13, 1882, p. 132, has given an empirical formula for calculating the relation between the volume, pressure, and temperature of a substance in both liquid and gaseous states. The equation he gives is a continuous one for an isothermal, and he determines the pressure at which evaporation takes place by considering that the work done in the transformation from liquid to gas at a constant pressure must be equal to what would be done if the transformation took place along the continuous isothermal. He requires, for convenience in applying this to actual cases, to calcu-

late the values of certain rather complicated exponential functions, and has published tables of their values which greatly facilitate the work of comparing his formula with observations of vapour-pressures at different temperatures. He has compared his formula with determinations of vapour-pressure, &c., by Andrews and Regnault of carbon dioxide, and by Regnault and Sajotschewsky of ether, and with Regnault's experiments on water, and has shown that they agree very well. He has also, by help of his formula, calculated the critical temperature for water, and finds it to be about  $332^{\circ}$  C., and the critical pressure to be 134 atmospheres.

Professor Ramsay has kindly furnished me with his and Mr. Young's observations on alcohol, and I have compared them with Clausius's formula, with which they agree very well.

The formula Clausius has given may be described as follows:—

The relation connecting the volume, pressure, and temperature of a substance can be expressed by the formula—

$$\frac{p}{RT} = \frac{1}{v-\alpha} - \frac{1}{\Theta(v+\beta)^2}.$$

In this  $R$ ,  $\alpha$ , and  $\beta$  are constants for each substance,  $p$  is the pressure,  $v$  the specific volume,  $T$  the absolute temperature, and  $\Theta$  is a function of the temperature which vanishes with  $T$ , and for which Clausius has given the formula—

$$\frac{* \Theta_c}{\Theta} = (1+b) \left( \frac{T_c}{T} \right)^n - b,$$

in which  $b$  and  $n$  are constants for any one substance, and  $T_c$  and  $\Theta_c$  the values of  $T$  and  $\Theta$  at the critical temperature.

From a consideration of the isothermals represented by Clausius's formula it is easy to show that the critical isothermal, for which two of the tangents parallel to the axis from which pressures are measured coincide, gives—

$$\Theta_c = \frac{8}{27(\alpha+\beta)}.$$

As the combination  $\alpha + \beta$  occurs frequently, Clausius denotes it by  $\gamma$ . He expresses the specific volumes of the saturated liquid and gas by  $\sigma$  and  $s$ , and uses  $w$  and  $W$  for  $\sigma - \alpha$  and  $s - \alpha$  respectively. He also uses the symbol  $\Pi = P/(RT)$  where  $P$  is the saturated vapour-pressure, and subscribes  $c$ , thus  $\Pi_c$ , to express the value of any of these quantities at the critical point. Hence we get—

\* There is a misprint of  $\frac{\Theta}{\Theta_c}$  for  $\frac{\Theta_c}{\Theta}$  on the last line of the text, formula 7, of p. 135 of Clausius's second paper in the 'Phil. Mag.,' vol. 13.

$$\Pi_c = \frac{1}{8\gamma} \qquad W_c = w_c = 2\gamma.$$

I have assumed as the result of observation that  $T_c = 516.5$  and  $P_c = 49,000$  mm. This latter value is probably a little too large, but, as there seems some uncertainty as to its value from the experiments, from which it is very difficult to approximate accurately to the actual position of the critical point, I have thought this value sufficiently accurate. I have calculated the result of making changes in this value, and any variation within limits allowable by the experiments does not materially affect my results.

The values of these constants for alcohol as determined from the observations are—

$$\begin{aligned} R &= 1351.35 \\ T_c &= 516.5 \\ P_c &= 49,000 \\ \alpha + \beta = \gamma &= 1.780 \\ W_c = w_c = 2\gamma &= 3.560 \\ \Pi_c = \frac{1}{8\gamma} &= 0.07023 \\ \Theta_c = \frac{8}{27\gamma} &= 0.1664 \\ b &= 0.9118 \\ n &= 1.3462 \end{aligned}$$

I have found that constant values for  $\alpha$  and  $\beta$  do not satisfy the observations accurately, and that  $\alpha$  varies from  $1.087$  at  $0^\circ$  C. to  $0.184$  at  $240^\circ$  C., as I explain further on. I calculated  $b$  and  $n$  so as to make the saturated vapour-tensions correct at  $0^\circ$  C. and  $100^\circ$  C. The process of calculation I adopted was to calculate  $\Pi/\Pi_c$  at  $0^\circ$  C. and  $100^\circ$  C., and then from Clausius's tables obtain the corresponding values of  $\Theta/\Theta_c$ . This gave two equations, to determine  $b$  and  $n$  by means of  $\Theta_c/\Theta = (1 + b)(T_c/T)^n - b$ . The equation for  $n$  being—

$$\frac{\Theta_c - 1}{\Theta_c - 1} = \frac{\left(\frac{T_c}{T}\right)^n - 1}{\left(\frac{T_c}{T'}\right)^n - 1}.$$

This was solved by trial and error and then  $b$  calculated. Having determined  $b$  and  $n$ , the value of  $\Theta/\Theta_c$  for any temperature may be easily calculated, and thence the corresponding values of  $\Pi/\Pi_c$ ,  $W/W_c$ ,

and  $w/w_c$  obtained by interpolation from Clausius's tables. From these  $P$ ,  $W$ , and  $w$  are calculated and compared with observation. It is from this comparison of  $w$  with the volume of the liquid at various temperatures and pressures that it is evident that  $\alpha$  is not constant, for the difference between  $w$  calculated and  $\sigma$  as observed is by no means so.

The following table exhibits some of my results :—

	0° C.	100° C.	200° C.	240° C.	242·5° C.	243·5° C.
P observed.....	12·24	1695	22434	46339	—	—
P calculated .....	12·24	1695	22106	46172	—	49000
W .....	30·210	284·5	19·09	5·43	4·26	3·56
$s$ .....	29·046	284·4	19·85	5·83	4·62	—
$w$ .....	0·177	0·389	1·003	2·43	2·99	3·56
$\sigma$ .....	1·264	1·390	1·796	2·614	2·925	—
$\sigma - w = \alpha$ .....	1·037	1·001	0·793	0·184	—0·065	—

In some of these cases, as for example for  $W$  at 0° C., it is very difficult to interpolate accurately into Clausius's tables, and similarly for the values of  $w$  near the critical point, and I consequently do not attribute much accuracy to these values. On the whole, however, I think that, considering the enormous range of values to be represented by the formula, it is most remarkably accurate. When we compare the calculated and observed volumes of the liquid, in which case  $\alpha$  is of importance, we find that no constant value for  $\alpha$  can make them agree, for  $\alpha$  obviously diminishes with increased temperature, and near the critical point the value of  $\alpha$  for the liquid and gaseous states is not the same. All this means of course that Clausius's formula does not apply accurately to the case of alcohol. Clausius has not, as far as I can find, applied his formula to calculate the volumes of liquids, and without doing so the want of constancy in  $\alpha$  would not appreciably affect the result. Messrs. Ramsay and Young have made observations of the volume of the liquid at various temperatures and pressures, and I have compared some of their results with the formula. In this way it can be seen that  $\alpha$  must be made a function of the pressure as well as of the temperature. I have calculated the values of  $v - \alpha$  at certain temperatures and pressures, and find at 110° C.—

Pressure.	2362	60,000
$v - \alpha$ (calculated) .....	0·409	0·383
$v$ (observed) .....	1·417	1·3925
$\alpha$ .....	1·008	1·0095

At 200° C.—

Pressure.	22,434.	60,000.
$v - \alpha$ (calculated) .....	1·003	0·858
$v$ (observed) .....	1·793	1·720
$\alpha$ .....	0·793	0·862

At 240° C.—

Pressure.	47,500.	60,000.
$v - \alpha$ (calculated) .....	2·166	1·641
$v$ (observed) .....	2·468	2·169
$\alpha$ .....	0·298	0·528

From this it is evident that  $\alpha$  diminishes with increased temperature, and increases with increased pressure.

Notwithstanding this, that Clausius's formula does not at all accurately represent the state of the liquid, there is no doubt that it gives a wonderfully accurate general representation of the more important features of the change of state. In this respect it is of enormously higher value than the formulæ that only give the relations connecting the temperature and pressure of saturated vapours. In addition to this, which it certainly gives in a rather complicated way, it gives the state of the liquid and gas before and after as well as during evaporation, and enables us to calculate points on the theoretical continuous isothermal connecting the liquid and gaseous states. I have calculated enough of these points to roughly sketch in these curves that cannot be made the subjects of experimental investigation

by the usual methods, owing to the instability of the states they represent.

Clausius's equation may be put into the following form by assuming  $p/(RT) = y$  and  $v - \alpha = x$ —

$$y(x + \gamma)^2 = (x + \gamma)^2 - \frac{x}{\Theta}.$$

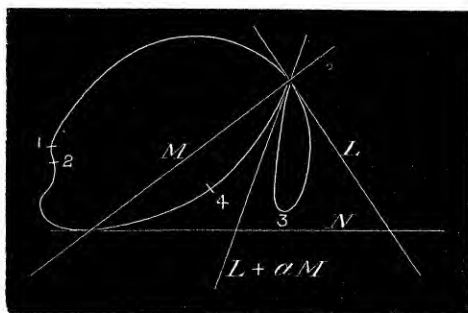
From this it is evident that an isothermal is a quartic curve having asymptotes  $y = 0$ ,  $x = 0$ , and  $x + \gamma$  a double asymptote at a cusp at infinity, so that the point at infinity on this line is a multiple point of a high order.

If we calculate the positions of the points of tangency of tangents parallel to  $y = 0$ , for which consequently  $dy/dx = 0$ , we have the cubic equation—

$$(x + \gamma)^3 = \frac{2x^2}{\Theta},$$

and when two of its roots are equal  $\Theta_c = \frac{8}{27\gamma}$ , and this determines the critical isothermal. The quartic consists of three branches. One, a serpentine branch, lies in the positive region of  $x$  and mostly of  $y$ , and is the only branch of physical interest at present. The other two branches lie entirely in the negative region of  $x$  and  $y$ . One of these is somewhat parabolic, and lies between  $x = 0$  and  $x = -\gamma$  asymptotic to both of them, the other is hyperbolic and asymptotic to  $x = -\gamma$  and to  $y = 0$ . The always real solution of the cubic that determines the points where  $dy/dx = 0$  for positive values of  $\Theta$  and  $\gamma$  is a point on the parabolic branch of the curve that lies between  $x = 0$  and  $x = -\gamma$ . The other two roots, when real, determine the highest and lowest points on the serpentine part of the curve that lies in the positive region of  $x$ . The accompanying diagram represents the general

FIG. 1

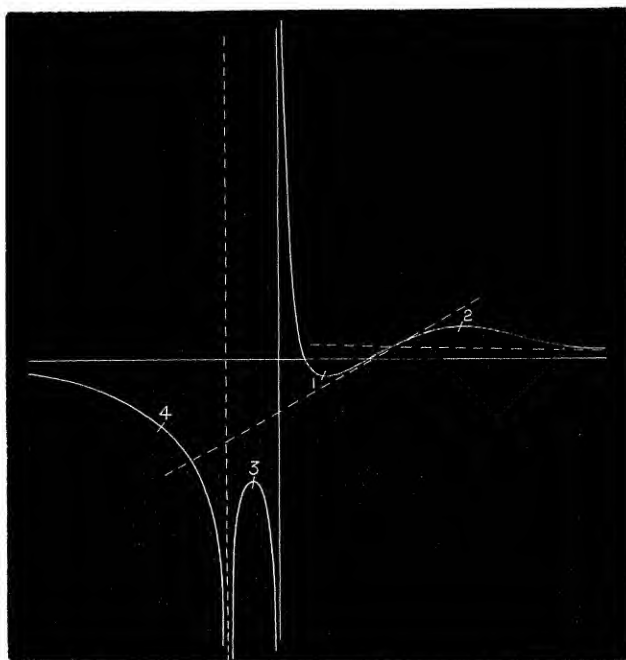


features of this class of curve. It is the particular case of the quartic—

$$(L + aM)^2(M^2 - LN) = bLM^3,$$

where  $L$ ,  $M$ , and  $N$  are lines in which  $M$  is the line infinity, and  $L$  and  $N$  are at right angles. In the general case this quartic is a continuous curve with a cusp at the intersection of  $L$  and  $M$  and  $L + aM$  as the cuspidal tangent, while  $L$  is a tangent to another branch that passes through the same point. Its general features are something like this—

FIG. 2.

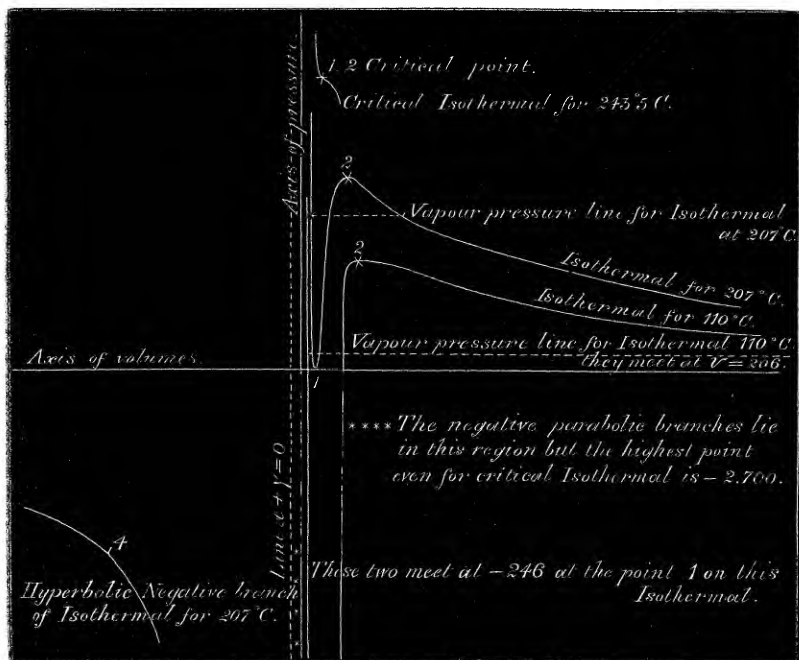


General Feature Diagram.

There is generally a double inflexion in the part of the curve outside the triangle  $L$ ,  $M$ ,  $N$ , and the particular one of a series of such curves for which the two inflexional tangents coincide is what corresponds to the critical isothermal in a gas. It is only what corresponds to the part outside the triangle that is of physical interest.

In the particular case of the curves representing the isothermals of alcohol, the negative parts of the curve lie at a very great distance

FIG. 3.



from the origin compared with the dimensions of the serpentine part of the positive branch, so that it is not easy to represent them both in the same figure. I have calculated several points on the isothermals corresponding to  $110^{\circ}\text{C}$ .,  $207.5^{\circ}\text{C}$ ., and  $243.5^{\circ}\text{C}$ .  $207.5^{\circ}\text{C}$  is the isothermal that just touches  $y = 0$ , while  $243.5^{\circ}\text{C}$  is the critical isothermal. The dotted lines represent the saturated vapour-tensions for which the areas included in the loops of the curve above and below are equal. The points numbered 1, 2, 3, 4 are specially noticeable points on the curves so numbered in the general feature diagrams.

The isothermal  $110^{\circ}\text{C}$ . goes down at the point 1 entirely outside the diagram to a pressure of  $-246,800\text{ mm.}$ , and intersects its vapour-pressure line outside the diagram to the right at a volume of 206. The negative parabolic branch of this isothermal only comes up at the point 3 to a pressure of  $-4,442,000\text{ mm.}$ , while the corresponding points of  $207.5^{\circ}\text{C}$ . and  $243.5^{\circ}\text{C}$ . come only to  $-4,044,000\text{ mm.}$  and  $-2,743,000\text{ mm.}$ , so that they are very far off. In the isothermal  $207.5^{\circ}\text{C}$ . the point 4 lies at about  $x = -32$ ,  $p = -32,000$ , so that it is not very far off.

What strikes me as most remarkable about these curves and other



than what one might have expected, is the very great distance to which the point 1 descends at ordinary temperatures. It would be interesting to compare the forms of these parts of the curve for several liquids, and see whether there was any connexion between it and the capillarity.

III. "The Influence of Stress and Strain on the Physical Properties of Matter. Part III. Magnetic Induction." By HERBERT TOMLINSON, B.A. Communicated by Professor W. GRYLLS ADAMS, M.A., F.R.S. Received March 17, 1887.

(Abstract.)

The author lays before the Society the results of experiments extending over a period of ten years on the effects of stress and strain on the magnetic permeabilities of iron, nickel, and cobalt.

Two methods were employed. In one the metal to be tested—usually in the form of wire—was placed with its axis coincident with that of a magnetising solenoid, in most cases of considerable length as compared with the diameter of the wire; round the central portion of the solenoid was wrapped a secondary coil. A similar pair of primary and secondary coils, with a similar piece of the same specimen of metal, was balanced against the first by means of resistance coils, so that on closing the magnetising circuit no deflection was produced in a delicate Thomson's galvanometer suitably connected up with the resistance coils and secondary coils. The alteration of magnetic permeability produced by stress was measured by the change necessary to be made in the resistance coils in order to restore the balance.

In the second method the resistance coils were dispensed with, and only a metal core used in one of the two pairs of solenoids which were connected in series each to each. The arrangements were such that the pairs of solenoids, when without any cores, balanced each other's effects on the galvanometer, so that the deflections of the latter instrument were due only to the magnetic permeability of the metal to be tested. The alteration of permeability was in this case measured by the change of deflection produced in the Thomson's galvanometer. The second method was the one principally employed.

In all cases, where it is advisable, the results are either given in C.G.S. units, or data are supplied for reducing to these units; moreover, the author has endeavoured to separate, as far as possible, the effects of stress on the *permanent* and on the *temporary* permeabilities of

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FIG. 2.



General Feature Diagram.

FIG. 3.

